

# Novel phase of beryllium fluoride at high pressure

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A previously unknown thermodynamically stable high-pressure phase of BeF<sub>2</sub> has been predicted using the evolutionary algorithm USPEX. This phase occurs in the pressure range 18–27 GPa. Its structure has *C2/c* space group symmetry and contains 18 atoms in the primitive unit cell. Given the analogy between BeF<sub>2</sub> and SiO<sub>2</sub>, silica phases have been investigated as well, but the new phase has not been observed to be thermodynamically stable for this system. However, it is found to be metastable and to have comparable energy to the known metastable phases of SiO<sub>2</sub>, suggesting a possibility of its synthesis.

**PACS numbers:**

## I. INTRODUCTION

Beryllium fluoride has many applications, such as coolant component in molten salt nuclear reactors<sup>1,2</sup>, production of special glasses<sup>3,4</sup>, manufacture of pure beryllium<sup>5</sup>, etc. Structurally, BeF<sub>2</sub> phases are similar to the phases of SiO<sub>2</sub> (Fig. 1):  $\alpha$ -quartz phase of BeF<sub>2</sub> and SiO<sub>2</sub> is stable from 0 to  $\sim 2$  GPa, and then transforms to coesite phase which persists up to  $\sim 8$  GPa, and then transforms to stishovite (rutile-type phase) in SiO<sub>2</sub><sup>6</sup>. However, the behavior of BeF<sub>2</sub> experimentally is not known for pressures above 8 GPa (see Scheme 1 in Ref.<sup>7</sup>).

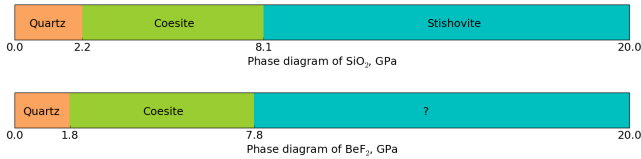


FIG. 1. Phase diagrams of SiO<sub>2</sub><sup>6</sup> and BeF<sub>2</sub><sup>7</sup> at low (up to room) temperatures.

One of our goals in present paper is to reveal which phase transitions can occur at higher pressures in BeF<sub>2</sub>. Beryllium compounds are extremely toxic for humans, and this limits experimentation. Computer simulation is a safe and cheap alternative to investigate such structures. In recent *ab initio* study<sup>8</sup> authors explored 13 well-known AB<sub>2</sub> structure types for their possible stability for BeF<sub>2</sub>:  $\alpha$ -quartz-type (*P3<sub>1</sub>21*),  $\beta$ -quartz-type (*P6<sub>2</sub>22*),  $\alpha$ -cristobalite-type (*P4<sub>1</sub>2<sub>1</sub>2*),  $\beta$ -cristobalite-type (*Fd-3m*), cubic CaF<sub>2</sub>-type (*Fm-3m*),  $\alpha$ -PbCl<sub>2</sub>-type (*Pnma*), Ni<sub>2</sub>In-type (*P6<sub>3</sub>/mmc*), coesite-type (*C2/c*), rutile-type (*P4<sub>2</sub>/mnm*), baddeleyite-type (*P2<sub>1</sub>/c*),  $\alpha$ -

PbO<sub>2</sub>-type (*Pbcn*),  $\alpha$ -CaCl<sub>2</sub>-type (*Pnnm*) and pyrite-type (*Pa-3*) structures. They found that the sequence of pressure-induced phase transitions of BeF<sub>2</sub> up to 50 GPa is as follows:  $\alpha$ -quartz-type  $\xrightarrow{0.59 \text{ GPa}}$  coesite-type  $\xrightarrow{6.47 \text{ GPa}}$  rutile-type  $\xrightarrow{24.94 \text{ GPa}}$   $\alpha$ -PbO<sub>2</sub>-type structures. Although BeF<sub>2</sub> under pressure has been theoretically investigated by Yu *et al.*<sup>8</sup>, we revisit these results to check for previously unknown structure(s), and we explore the relevance of these findings for SiO<sub>2</sub>.

## II. COMPUTATIONAL DETAILS

Computer simulations of BeF<sub>2</sub> and SiO<sub>2</sub> has been performed in two steps: (1) prediction of a new structure of BeF<sub>2</sub> using USPEX evolutionary algorithm; (2) calculation of properties of BeF<sub>2</sub> and SiO<sub>2</sub> in the wide range of pressures from 0 to 50 GPa with a 1 GPa step using DFT.

To find stable lowest-energy crystals structures, we performed fixed-composition search of the BeF<sub>2</sub> system at different pressures (15, 20 and 25 GPa) using the USPEX code<sup>9–11</sup>, in conjunction with first-principles structure relaxations using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)<sup>12</sup>, as implemented in the VASP package<sup>13</sup>. We employed projector augmented wave (PAW)<sup>14</sup> potentials with 2 valence electrons for Be and 7 — for F. The wave functions were expanded in a plane-wave basis set with the kinetic energy cutoff of 600 eV and  $\Gamma$ -centered meshes for Brillouin zone sampling with reciprocal space resolution of  $2\pi \times 0.10 \text{ \AA}^{-1}$ .

We used the VASP package to carefully reoptimize the obtained structures before calculating phonons, elasticity, electronic density of states (DOS), hardness of

BeF<sub>2</sub> and SiO<sub>2</sub>. For these relaxations, we also used the plane-wave cutoff of 600 eV and  $k$ -meshes with resolution of 0.10 Å<sup>-1</sup>. Phonons calculations have been performed using Phonopy<sup>15</sup> and Quantum Espresso<sup>16</sup> codes for the relaxed structures at pressures where these structures are found to be thermodynamically stable. Hardness was calculated using 3 methods: Lyakhov-Oganov model<sup>17</sup> based on the strength of bonds between atoms and bond network topology, Chen-Niu model<sup>18</sup> which uses elastic constants obtained from DFT calculations and Mukhanov-Kurakevych-Solozhenko thermodynamic model of hardness<sup>19</sup>.

### III. RESULTS AND DISCUSSION

USPEX allowed us to find a new structure of BeF<sub>2</sub>, stable at 18–27 GPa (Fig. 2). The structure has  $C2/c$  space group and contains 12 formula units in the Bravais cell (6 in the primitive cell) with  $a=8.742$  Å,  $b=8.695$  Å,  $c=4.178$  Å and  $\beta=66.1^\circ$  (at 20 GPa). Calculated density of this new  $C2/c$  phase is 4.2% higher than density of coesite phase, both at 20 GPa. For reference, here are lattice parameters for BeF<sub>2</sub>-stishovite at 30 GPa:  $a=b=3.986$  Å,  $c=2.501$  Å and  $\alpha=\beta=\gamma=90^\circ$ . The value of the bulk modulus  $B_0=22.4$  GPa of the  $C2/c$  structure of BeF<sub>2</sub> with its pressure derivative  $B'_0=3.9$  was obtained from a least-squares fit using the Murnaghan equation of state<sup>20</sup> (Fig. 3). The zero-pressure unit cell volume was taken as  $V_0=213.7$  Å<sup>3</sup>.

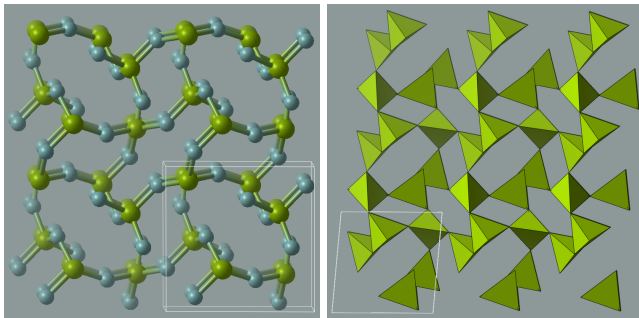


FIG. 2.  $C2/c$  structure of BeF<sub>2</sub>, stable at 18–27 GPa.

#### A. Thermodynamic stability

We have calculated the enthalpies of  $\alpha$ -quartz ( $P3_221$ ), coesite ( $C2/c$ ), coesite-II ( $C2/c$ ), stishovite ( $P4_2/mnm$ ),  $\alpha$ -PbO<sub>2</sub>-type ( $Pbcn$ ) structure and our new structure ( $C2/c$ ) for both BeF<sub>2</sub> and SiO<sub>2</sub> at different pressures from 0 to 50 GPa with a 1 GPa step. The results are presented in Fig. 4.

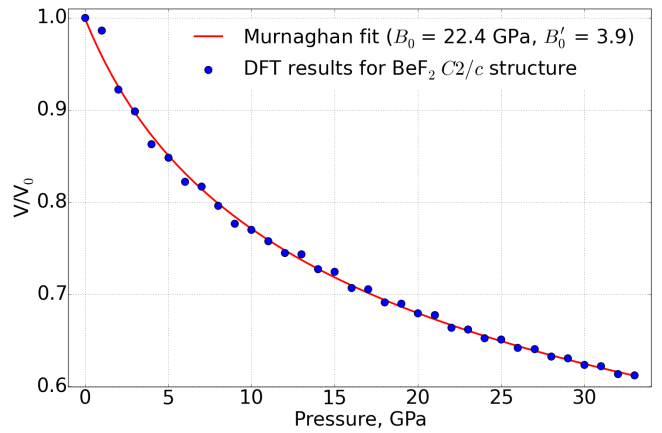


FIG. 3. Equation of state of BeF<sub>2</sub>  $C2/c$  structure.

#### 1. BeF<sub>2</sub> under pressure

For the case of BeF<sub>2</sub>  $\alpha$ -quartz structure is stable from 0 to 4 GPa, followed by coesite structure stable from 4 to 18 GPa, and the  $C2/c$  structure is found to be stable between 18 and 27 GPa, which then gives place to stishovite structure at higher pressures (Fig. 4(a)). We see transition from coesite-type to  $C2/c$ , then to rutile-type, but at much higher pressure (27 GPa against 6.47 GPa in Ref.<sup>8</sup>, where LDA was used). According to Demuth *et al.*<sup>21</sup>, the LDA approximation used in Ref.<sup>8</sup> underestimates phase transition pressures, whereas using the GGA yields more reliable results. The  $\alpha$ -PbO<sub>2</sub>-type structure is not stable at any pressure (in the investigated interval from 0 to 50 GPa) for BeF<sub>2</sub> (though it is close to stability at  $\sim 27$  GPa), while for SiO<sub>2</sub> it is indeed stable at pressures above  $\sim 80$ –90 GPa<sup>22</sup>.

#### 2. SiO<sub>2</sub> under pressure

From Fig. 4(b) it is clearly seen that in SiO<sub>2</sub> the transition from  $\alpha$ -quartz to coesite occurs at 5 GPa, followed by transformation to stishovite at  $\sim 7$  GPa, which continues to be stable up to 50 GPa. This phase transition sequence is in good agreement with experiments<sup>6</sup> and with the GGA results by Demuth *et al.*<sup>21</sup>, Oganov *et al.*<sup>22</sup> and LDA results of Tsuchiya *et al.*<sup>23</sup>; it is known though<sup>21</sup> that the GGA is more accurate than the LDA for phase transition pressures. The new structure is not stable at any pressure for SiO<sub>2</sub>, but at 0 GPa is only 3.4 meV/atom higher in energy than  $\alpha$ -quartz, and should be synthesizable as a metastable phase. Our results of coesite  $\rightarrow$  coesite-II transition are in good agreement with recent study of Černok *et al.*<sup>24</sup>, where they observe coesite at 20.3 GPa, and after an abrupt change in the diffraction pattern between  $\sim 20$  and  $\sim 28$  GPa — coesite-II at 27.5 and 30.9 GPa.

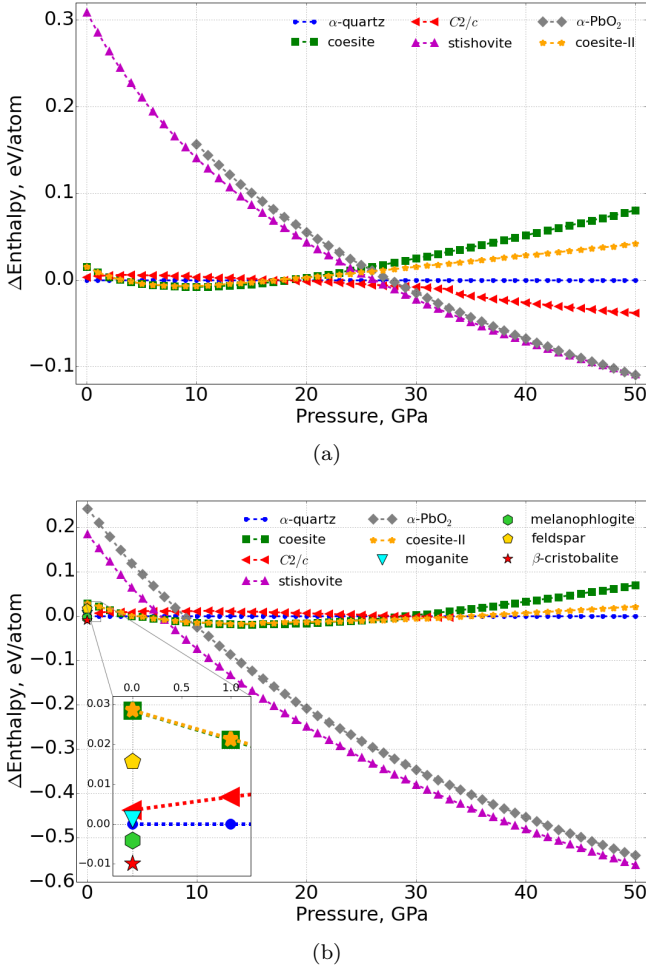


FIG. 4. Enthalpies (relative to  $\alpha$ -quartz) of (a)  $\text{BeF}_2$  and (b)  $\text{SiO}_2$  phases as a function of pressure.

### 3. Metastable structures of $\text{SiO}_2$

It is well known that  $\text{SiO}_2$   $\alpha$ -quartz is thermodynamically stable at ambient pressure. However, there are numerous known  $\text{SiO}_2$  polymorphs which are metastable, but exist in nature or can be synthesized. We examined  $\text{SiO}_2$  feldspar, baddeleyite, melanophlogite and moganite at 0 GPa. El Goresy *et al.*<sup>25</sup> claimed a baddeleyite-like post-stishovite phase of silica in the Shergotty meteorite, however later that controversial phase turned out to be  $\alpha$ - $\text{PbO}_2$ -like silica<sup>26</sup>. Our calculations confirm that the baddeleyite-like form of  $\text{SiO}_2$  is very unfavorable at 0 GPa and spontaneously (barrierlessly) transforms into the  $\alpha$ - $\text{PbO}_2$ -like structure. We have found that  $\text{SiO}_2$ -feldspar, moganite and melanophlogite are energetically very close to the stable phase ( $\alpha$ -quartz) and to the new  $C2/c$  structure. Differences in enthalpy between melanophlogite, new structure and  $\alpha$ -quartz are less than 0.01 eV/atom (see zoomed inset in Fig. 4(b)). The fact that complex open structure of melanophlogite (138 atoms/cell) has a slightly lower energy than  $\alpha$ -

quartz, can be explained by errors of the GGA, which were discussed in details by Demuth *et al.*<sup>21</sup>. They also found  $\beta$ -cristobalite (Fig. 4(b)) is lower in energy by about 0.03 eV/ $\text{SiO}_2$  than  $\alpha$ -quartz, confirmed by calculations of Zhang *et al.*<sup>27</sup>, showing that the GGA slightly overstabilizes low-density structures.

## B. Lattice dynamics

Since the new structure of  $\text{BeF}_2$  appears to be thermodynamically stable, analysis of dynamical stability (phonon dispersion) has been performed for this structure as well as for all other structures at pressures where they were found to be thermodynamically stable. Our results show that  $\text{BeF}_2$   $\alpha$ -quartz at 0 GPa, coesite at 5 GPa, new structure at 25 GPa and stishovite at 30 GPa do not have imaginary frequencies. Similar results are observed for  $\text{SiO}_2$   $\alpha$ -quartz at 0 GPa, coesite at 5 GPa and stishovite at 10 GPa. Fig. 5 shows dynamical stability of the new structure of  $\text{BeF}_2$  since no imaginary frequencies are observed in the phonon dispersion plot.

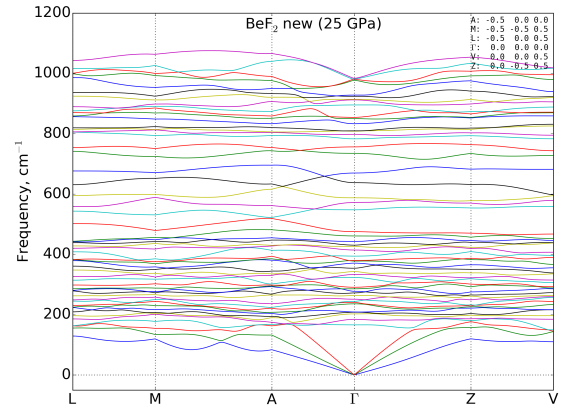


FIG. 5. Phonons dispersion curves showing dynamical stability of the  $C2/c$  structure of  $\text{BeF}_2$  at 25 GPa.

## C. Electronic properties

According to Fig. 6, all  $\text{BeF}_2$  phases are insulators, the DFT band gap increases from  $\sim 7$  to  $\sim 10$  eV with increasing pressure from 0 to 30 GPa and the value of the gap is in good agreement with data of Yu *et al.*<sup>8</sup>.

For  $\text{SiO}_2$  (Fig. 7) we also observe insulating behavior, and the band gap is about 6 eV and remains almost unchanged with increasing pressure.

## D. Hardness

Three models have been exploited to calculate hardnesses — the Lyakhov-Oganov<sup>17</sup>, Chen-Niu<sup>18</sup> and

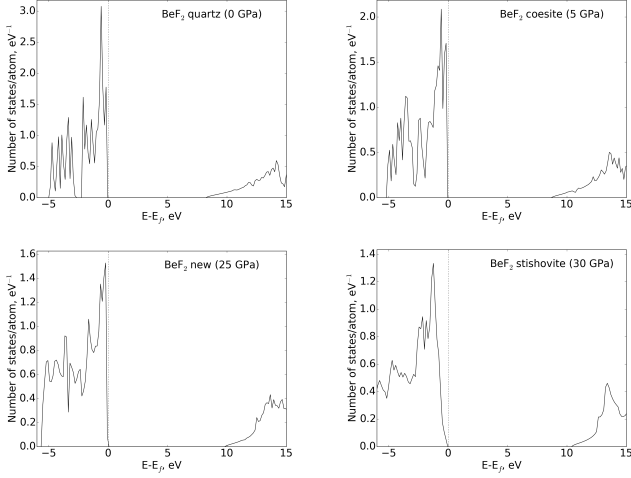


FIG. 6. Density of states of  $\text{BeF}_2$  in the  $\alpha$ -quartz (at 0 GPa), coesite (at 5 GPa),  $C2/c$  structure (at 25 GPa), and stishovite (at 30 GPa) phases.

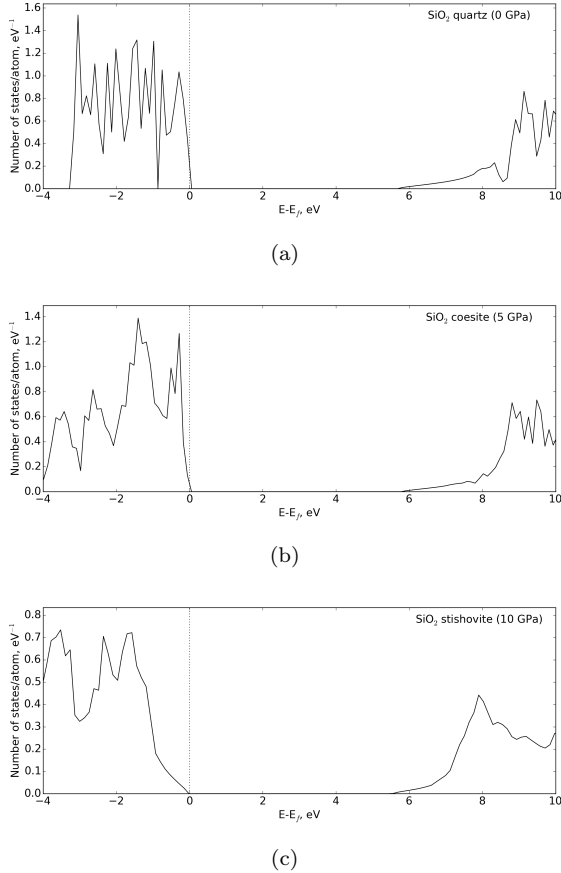


FIG. 7. Density of states of  $\text{SiO}_2$  in the (a)  $\alpha$ -quartz (at 0 GPa), (b) coesite (at 5 GPa) and (c) stishovite (at 10 GPa) phases.

Mukhanov-Kurakevych-Solozhenko<sup>19</sup> models. First approach is based on concepts of bond strengths and bond topology to compute hardness. Detailed description of the methodology can be found in Ref.<sup>17</sup>. This model has been implemented in the USPEX code, and for greater convenience has also been implemented as an online utility available at <http://han.ess.sunysb.edu/hardness/>. The second method of hardness calculation is Chen-Niu model, which is based on elastic tensor components and also implemented in the USPEX code. The third one is a thermodynamic model of hardness.

The results can be seen in Table I. Experimental data are provided where available — Vickers hardness of  $\text{SiO}_2$ -quartz<sup>28</sup>,  $\text{SiO}_2$ -coesite<sup>19</sup> and  $\text{SiO}_2$ -stishovite<sup>29</sup>. From Table I it is clearly seen that the calculated hardness of  $\text{SiO}_2$  quartz and stishovite is much higher than one of  $\text{BeF}_2$  analogs. The hardness of  $\text{BeF}_2$  and  $\text{SiO}_2$  in the new  $C2/c$  structure is comparable with the hardness of  $\alpha$ -quartz and coesite.

#### IV. CONCLUSIONS

We have examined thermodynamic, vibrational, electronic and elastic properties of  $\text{BeF}_2$  and  $\text{SiO}_2$  phases using DFT calculations. The sequence of pressure-induced phase transitions of  $\text{BeF}_2$  up to 50 GPa is as follows:  $\alpha$ -quartz-type  $\xrightarrow{4 \text{ GPa}}$  coesite-type  $\xrightarrow{18 \text{ GPa}}$   $C2/c$   $\xrightarrow{27 \text{ GPa}}$  stishovite (rutile-type) structures. We found a new phase of  $\text{BeF}_2$  which is thermodynamically stable at pressures from 18 to 27 GPa. This phase is not observed in  $\text{SiO}_2$ , but could be synthesized in principle. Electronic properties analysis has shown  $\text{BeF}_2$  and  $\text{SiO}_2$  remain insulating in a wide range of pressures (from 0 to 50 GPa). Hardness of  $\text{BeF}_2$  and  $\text{SiO}_2$  in the new structure is comparable with hardness of  $\alpha$ -quartz and coesite at 0 GPa. Hardnesses of metastable  $\text{SiO}_2$  structures have been examined as well.

#### V. AUTHOR CONTRIBUTIONS

M.R., H.N. and M.D. performed the calculations, M.R. and A.R.O. contributed to the analysis and wrote the paper. X.F.Z and G.R.Q. provided technical assistance with calculations. V.L.S. proposed the idea, performed calculations of hardness and participated in the discussion.

#### VI. ADDITIONAL INFORMATION

Competing financial interests: The authors declare no competing financial interests.

TABLE I. Hardness of BeF<sub>2</sub> and SiO<sub>2</sub> structures at 0 GPa in GPa. For the metastable SiO<sub>2</sub> structures we present enthalpies relative to  $\alpha$ -quartz (in eV per formula unit).

	BeF <sub>2</sub>			SiO <sub>2</sub>		
	Lyakhov-Oganov	Chen-Niu	Mukhanov <i>et al.</i> <sup>a</sup>	Lyakhov-Oganov	Chen-Niu	Experiment
Quartz	7.1	7.5	11.0	20.0	12.5	12.0 <sup>b</sup>
Coesite	8.2	8.3	11.7	22.3	8.4	20.0 <sup>b</sup>
New structure	7.3	6.8	13.5	19.1	6.7	—
Stishovite	8.2	12.7	15.1	29.0	28.7	33.0 <sup>b</sup>
Metastable structures (SiO <sub>2</sub> only):						
	Relative enthalpy, eV/f.u.			Hardness, GPa		
				Lyakhov-Oganov model	Chen-Niu model	
Feldspar	0.047			6.7		11.8
Baddeleyite	0.726			29.6		28.0
Melanophlogite	−0.013			12.5		3.3
Moganite	0.003			19.5		12.8

<sup>a</sup> Thermodynamic model of hardness (Ref.<sup>19</sup>)

<sup>b</sup> Vickers hardness

## ACKNOWLEDGMENTS

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## Appendix A: Densities of BeF<sub>2</sub> and SiO<sub>2</sub> structures

Table II shows densities of BeF<sub>2</sub> structures at 0 and 20 GPa and SiO<sub>2</sub> structures at 0 GPa.

TABLE II. Densities of BeF<sub>2</sub> and SiO<sub>2</sub> structures.

System	Number of atoms	Volume, Å <sup>3</sup> /cell	Density, g/cm <sup>3</sup>
<b>BeF<sub>2</sub> at 0 GPa:</b>			
$\alpha$ -quartz	9	105.167	2.244
coesite	24	254.636	2.472
coesite-II	96	1021.960	2.464
C2/c	18	213.696	2.209
stishovite	6	47.771	3.294
<b>BeF<sub>2</sub> at 20 GPa:</b>			
$\alpha$ -quartz	9	73.078	3.230
coesite	24	202.001	3.116
C2/c	18	145.159	3.252
stishovite	6	41.492	3.793
<b>SiO<sub>2</sub> at 0 GPa:</b>			
$\alpha$ -quartz	9	116.934	2.580
coesite	24	283.341	2.839
coesite-II	96	1137.296	2.830
C2/c	18	243.569	2.477
stishovite	6	48.185	4.174
$\alpha$ -PbO <sub>2</sub> -type	12	94.623	4.251

## Appendix B: CIF file of BeF<sub>2</sub> C2/c structure at 20 GPa

```
# CIF file
# This file was generated by FINDSYM (H.T. Stokes)

data_findsym-output

_symmetry_space_group_name_H-M 'C 1 2/c 1'
_symmetry_Int_Tables_number 15

_cell_length_a      8.74241
_cell_length_b      8.69478
_cell_length_c      4.17800
_cell_angle_alpha   90.00000
_cell_angle_beta    66.07927
_cell_angle_gamma   90.00000

loop_
_space_group_symop_operation_xyz
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-x,-y,-z
x,-y,z+1/2
x+1/2,y+1/2,z
-x+1/2,y+1/2,-z+1/2
-x+1/2,-y+1/2,-z
x+1/2,-y+1/2,z+1/2

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Be1 Be  0.30175  0.08755  0.27471  1.00000
Be2 Be  0.00000  0.18404  0.25000  1.00000
F1  F  -0.11350  0.09592  0.11433  1.00000
F2  F   0.14707  0.43232  0.42082  1.00000
F3  F  -0.11681  0.27080 -0.42582  1.00000
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